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12a. DISTRIBUTION / AVAILABILITY STATEMENT

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13. ABSTRACT *(Maximum 200 words)*

Polyphosphazenes are a new polymers with unique properties which include a combination of high temperature stability, low temperature flexibility, low surface energy, biofriendliness, and inflammability. We focused our research on polymerization of phosphoranimines catalyzed by Lewis acids and Lewis bases and synthesis of poly(diarylphosphazenes) by silyl azide intermediates and characterized the new polymers and copolymers using various techniques. The catalyzed polymerization of phosphoranimineshas been successfully used for the synthesis of random copolymers and the first block copolymers between two different polyphosphazenes. Additonally, we prepared polyphosphazene-organic polymer diblock structures using macromolecular phosphoranimines. The second part of the research was devoted to the preparation of new branched and hyperbranched polymers by controlled radical polymerization. We used atom transfer radical polymerization (ATRP) to prepare hyperbranched polystyrenes and polyacrylates. In addition, the novel class of compounds being simultaneously monomers and initiators (AB* monomers or inimers) were used successfully to design and prepare polymers and copolymers with novel topologies, compositions and functionalities. We prepared first molecular bottle-brush structures, multiarm star block and star diblock copolymers and also novel polar thermoplastic elastomers by entirely radical processes.

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Synthesis, Characterization and Potential Applications of New Materials from Functionalized Polyphosphazenes

FINAL REPORT

Krzysztof Matyjaszewski

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A. Statement of the problem studied

Polyphosphazenes are a new polymers with unique properties which include a combination of high temperature stability, low temperature flexibility, low surface energy, biofriendliness, and inflammability. The classic synthetic approach provides very high molecular weight polymers with broad polydispersities and with no control of end groups in low yields and under extreme conditions (a few days at temperatures above 200 ^{o}C in a highly corrosive medium). The purpose of the project investigated in our laboratories was to develop alternative routes to polyphosphazenes with control of molecular weights, polydispersities, tacticities and terminal functionalities. Especially the functionalized polyphosphazenes could be used to prepare novel hybrid materials with conventional organic polymers.

In addition, we simultaneously studied new synthetic routes towards branched and hyperbranched organic and inorganic polymers. This research was the main focus of our work during the last year of the project supported by ARO.

B. Summary of the most important results

We focused our research on polymerization of phosphoranimines catalyzed by Lewis acids and Lewis bases and synthesis of poly(diarylphosphazenes) by silyl azide intermediates. In addition to the synthesis, we characterized the new polymers and copolymers using various techniques including SEC, NMR, UV, VT SAXS and WAXS, X ray, electron diffraction, DSC, TGA, DMA, and dielectric relaxation. As discovered in our laboratories, the polymerization of phosphoranimines catalyzed by nucleophiles under mild conditions gives linear polyphosphazenes with low polydispersities ($M_w/M_n<1.5$), moderate and tunable molecular weights ($M_n \approx 10{,}000$ to 200,000) and controlled end groups. It has been also shown that the catalyzed polymerization of phosphoranimines can be successfully used for the synthesis of random copolymers and the first block copolymers between two different polyphosphazenes. Additonally we were able to regulate molecular weights by adding various alkyl and macromolecular phosphoranimines as chain stoppers. The resulting products included block copolymers, first example of the polyphosphazene-organic polymer diblock structures.

The second part of the research was devoted to the preparation of new branched and hyperbranched polymers by controlled radical polymerization. We used atom transfer radical polymerization (ATRP) to prepare hyperbranched polystyrenes and polyacrylates. In addition, the novel class of compounds being simultaneously monomers and initiators (AB* monomers or inimers) was used successfully to design and prepare polymers and copolymers with novel topologies, compositions and functionalities. We prepared first molecular bottle-brush structures, multiarm star block and star diblock copolymers and also novel polar thermoplastic elastomers by entirely radical processes.

C. LIST OF MANUSCRIPTS PUBLISHED UNDER ARO SPONSORSHIP

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10. "Preparation of Hyperbranched Polyacrylates by Atom Transfer Radical Polymerization: 1. Acrylic AB* Monomers in "Living" Radical Polymerization", S. G. Gaynor, M. Podwika, K. Matyjaszewski, *Macromolecules,* 30, 5192 (1997)

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1. "Mechanistic Aspects of Atom Transfer Radical Polymerization", K. Matyjaszewski, *ACS Symp. Series*, 685, 258 (1998)

2. " How to Make Polymer Chains of Various Shapes, Compositions, and Functionalities by Atom Transfer Radical Polymerization (ATRP)", K. Matyjaszewski, S. G. Gaynor *ACS Symp. Series*, 685, 396 (1998)

D. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:

Personel supported during the reported period:
Principal investigator: K. Matyjaszewski
Graduate students: M. White, S. Gaynor, J. Sarver, K. Beers, S. Arehart
Undergraduate students: Shane Edelman, Tony Kulfan, Allison Kern, Matt Podwika

Degrees: M. White (Ph.D.), S. Gaynor (Ph.D.)
S. Edelman (B.S.), Tony Kulfan (B.S.)

Honors and Awards:
1. K. Matyjaszewski received Carl S. Marvel Creative Polymer Chemistry Award administered by Polymer Division of the American Chemical Society
2. Scott Gaynor received a William Bradbury Award administered by Plastic Institute of America

E. REPORTABLE INVENTIONS:
Two patent applications have been filed on behalf of Carnegie Mellon University for novel polymer topologies prepared by ATRP from AB* monomers.